

FRONTIER MOLECULAR ORBITAL CALCULATION AND ITS RELATION WITH THE TWO-PHOTON ABSORPTION CROSS-SECTIONS OF PERYLENE COMPOUNDS.

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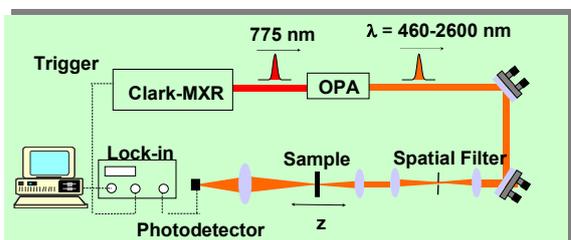
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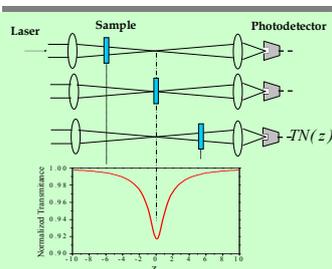
Abstract

Knowledge about nonlinear absorption spectra of materials used in photonic devices is of paramount importance in determining their optimum operation wavelengths. In this work, we have investigated the two-photon absorption (2PA) degenerate cross-section spectrum for perylene derivatives using the Z-scan technique with femtosecond laser pulses. All perylene derivatives studied present large 2PA cross-sections, only comparable to the best ones reported in the literature. Aiming to search for a close relation between the extremely large 2PA cross-sections of the perylene derivatives and their molecular structures and charge distribution, frontier molecular orbital calculations (HOMO and LUMO) were performed using semi-empirical methods.

✓ Z-Scan experimental setup and typical results



Our Z-scan experiment employs laser pulses from a commercial optical parametric amplifier (TOPAS) pumped by a 150 fs pulses at 775 nm delivered by a Ti:sapphire chirped pulse amplified system (CPA-2001, from Clark-MXR Inc.), operating at 1kHz repetition rate. The FWHM pulse duration from OPA was about 120 fs, and the spatial profile of the laser beam presented an approximately Gaussian distribution.



Typical curve of 2PA. The fit are obtained by:

$$T(z) = \frac{1}{1 + (z/z_0)^2} \ln[1 + q_0(z,0)e^{-z^2}]$$

$$q_0(z,t) = \beta I_0(t) L (1 + z^2/z_0^2)^{-1}$$

$$\delta = h\nu\beta/N$$

✓ The perylene compounds

PTCD are organic dyes, readily available, and thermal and chemically stable. The perylene moiety presents remarkable electron donor characteristics, although adding lateral groups in the molecule could play the role of electron acceptor or donor. Moreover, its strong absorption and emission in the visible spectral range make it as potential candidates for applications as photoconductors, laser materials, etc.

✓ Frontier molecular orbitals

The molecular geometries were optimized by the AM1 method.

Frontier molecular orbitals were calculated using ZINDO/S (HiperChem 7.5). Configuration interaction (CI) calculations included single excited configurations from the ground state, 24 (occupied) x 24 (unoccupied)

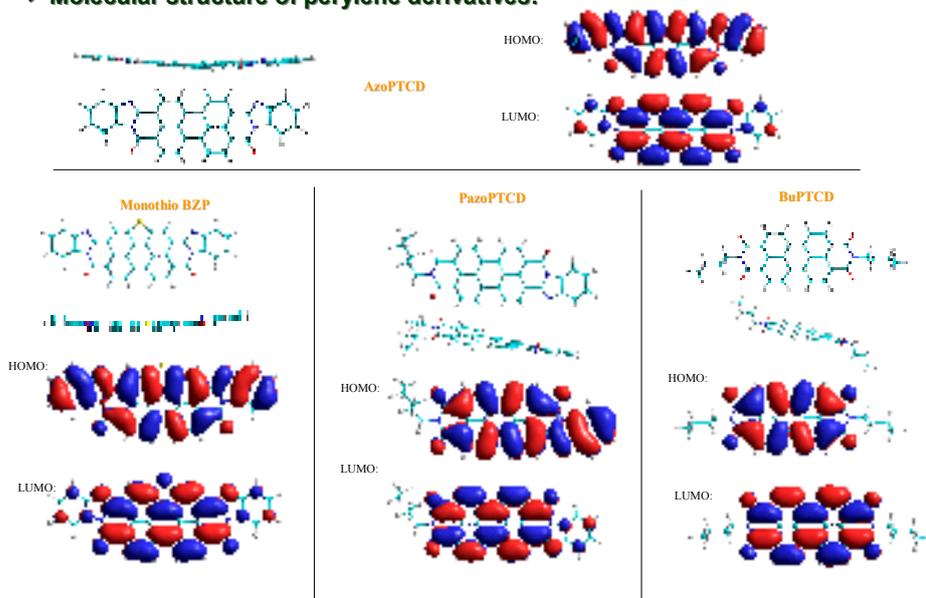
Transition energy ($DE_{\text{linear,abs}}$) decreases in a similar way as the π -conjugation length;

Bathochromic shift are the result of the HOMO \rightarrow LUMO energy change;

By analyzing the 2PA spectra far from linear absorption edge of the four PTCD derivatives, it can be established an unambiguous relation between molecular charge delocalization (conjugation length) and the third-order nonlinear optical response (2PA):

The results suggest that even larger 2PA cross-sections could be obtained by manipulating the perylene derivatives, by positioning donor or acceptor groups symmetrically or by increasing the molecule conjugation length, in agreement with the molecular design strategies proposed in the literature.

✓ Molecular structure of perylene derivatives:

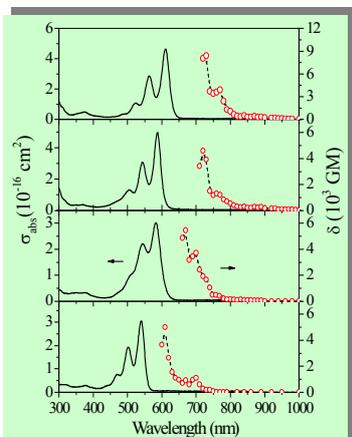


✓ Conclusions

The nonlinear absorption spectra of a family of perylene tetracarboxylic derivatives (PTCD) were determined using the open aperture Z-scan technique. A sum-over-states (SOS) model was employed to fit the experimental data providing an accurate description of the nonlinearity resonant enhancement and the other features of nonlinear spectra. The geometry optimization carried out using a semi-empirical method revealed that all the PTCDs have a central planar chromophore. Furthermore, the frontier molecular orbitals present similar features, indicating that nonlinear optical properties in PTCDs are mainly determined by the central portion of the molecule, with minimal effect from the lateral side-groups.



Linear absorption and degenerate 2PA spectrum of the PTCD materials in a solution with 10% trifluoroacetic acid in dichloromethane.



- PTCD \rightarrow linear absorption bands (400-660 nm), with the vibronic structure superposed to the π - π^* transition.

- High δ values at several excitation wavelengths.

- The increase observed in the 2PA cross-section spectra \rightarrow resonance enhancement of the nonlinearity \leftrightarrow sum-over states (SOS) model, assuming that the π - π^* transition gives the major contribution.

